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**THE ROLE OF VANADIUM CARBIDE TRAPS
IN REDUCING THE HYDROGEN EMBRITTLEMENT
SUSCEPTIBILITY OF HIGH STRENGTH ALLOY STEELS**

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INTRODUCTION

It is well-known that minor changes in chemistry can profoundly affect how well carbon and alloy steels resist hydrogen embrittlement. In some cases, these chemistry changes affect the steel's strength by altering heat treatability. (It is generally understood that increasing strength levels reduces steel's resistance to this phenomenon.) In other cases, however, steels of equivalent strength show a considerable range of susceptibility. For example, Raymond suggested that minor elemental additions of silicon or vanadium reduced steel's susceptibility to hydrogen embrittlement (ref 1). It has also been suggested that the effects of minor alloy additions could be associated with the number, types, and binding energies of hydrogen to traps in the metal matrix (refs 2, 3). These traps can be dislocations (refs 4-7), grain boundaries (refs 8-10), voids (refs 11, 12), or particle matrix interfaces (refs 5, 8, 13). Alloying elements with a strong affinity for hydrogen can also act as effective traps (ref 14). The traps effectively prevent hydrogen from migrating to highly stressed regions in an alloy where they can either initiate or propagate cracks. The traps both reduce the total amount of diffusible hydrogen and redistribute hydrogen in the alloy.

The purposes of this study were to examine how carbon and vanadium affect the hydrogen embrittlement susceptibility of alloy steels and to determine the role of these alloying elements.

EXPERIMENTAL PROCEDURE

Materials

Experiments were performed on commercial and modified heats of quenched and tempered ASTM A723 and AISI 4340 alloy steels. Specimens were heat-treated, austenitized at 840°C (1550°F) for 1 hour, water quenched, and tempered for 1 hour at 232°C (450°F) to approximately the same yield and tensile strengths shown in Table 1.

Table 1. Mechanical Properties

| Alloy | Mean Yield Strength | Mean Ultimate Tensile Strength |
|---------------|----------------------------|---------------------------------------|
| A723 Base | 1448 MPa (210.0 Ksi) | 1800 MPa (261.0 Ksi) |
| 4340 Base | 1579 MPa (229.7 Ksi) | 1860 MPa (269.7 Ksi) |
| A723 Modified | 1586 MPa (230.9 Ksi) | 1923 MPa (278.9 Ksi) |
| 4340 Modified | 1572 MPa (228.0 Ksi) | 1862 MPa (270.0 Ksi) |

The chemistries of each alloy are shown in Table 2. The principal differences in chemistry include a 0.06 wt. % lower carbon level for the A723 alloy compared to the 4340 alloy and small differences in chromium, nickel, and molybdenum. In addition, the A723 alloy contains approximately 0.12 wt. % vanadium. The amount of sulfur—which often has a large effect on the mechanical properties of carbon steels—is not significantly different between the A723 (with sulfur at 0.011%) and the 4340 (with sulfur at 0.013%). Therefore, in this case, sulfur is not considered to cause a difference in hydrogen embrittlement susceptibility.

Table 2. Chemistries (Wt. %)

| | A723 | 4340 |
|----|-------------|-------------|
| C | 0.34 | 0.40 |
| S | 0.011 | 0.013 |
| P | 0.010 | 0.013 |
| Mn | 0.59 | 0.74 |
| Cr | 0.96 | 0.76 |
| Ni | 2.50 | 1.71 |
| Mo | 0.39 | 0.23 |
| V | 0.12 | 0.006 |
| Si | 0.26 | 0.25 |

Alloy Modification

Two experimental laboratory melts were produced to compare the elemental effects of carbon and vanadium on the hydrogen embrittlement of these steels. Modified A723 was prepared with a carbon level of 0.40%, which is equivalent to that of 4340 steel. Modified 4340 was prepared with a vanadium level of 0.12%, which is equivalent to that of A723 steel. The alloy chemistries were modified by adding base alloys to the melts—thereby producing 13.6 kg (30 lbs.) samples of the new alloy, which were then remelted in an electric furnace and poured into small ingots. The cast ingots were then forged at 1090°C (2000°F) into 16 mm (0.625 in.) square bars (for a forging reduction of 2.5) and heat-treated to the strength levels shown in Table 1. After heat treatment, the blanks were machined into 9.0 mm (0.357 in.) diameter tensile bars (per ASTM E-8) that had a 60° notch with a root diameter of 6.35 mm (0.250 in.) (Figure 1).

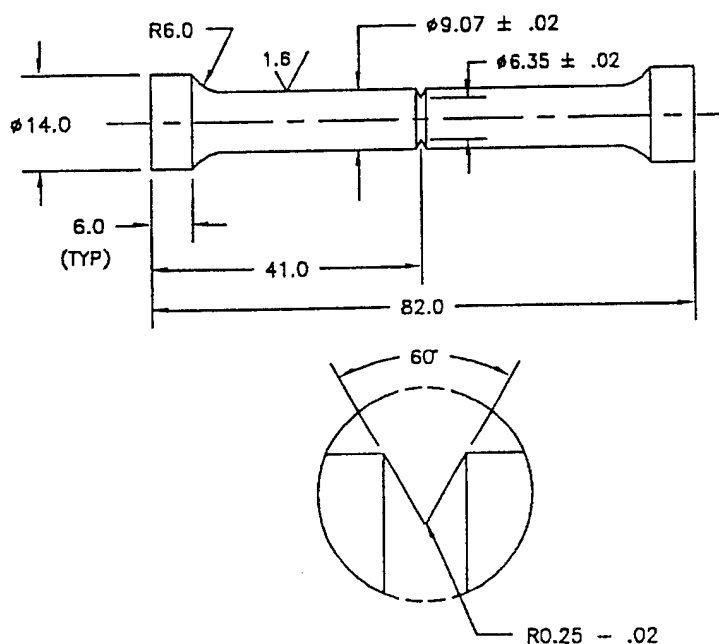


Figure 1. Notched tensile bar

Electrolytic Charging of Hydrogen

The specimens were electrolytically charged with hydrogen. The notch tensile bars were connected as cathodes in a 10% H₂SO₄ solution that contained 0.3 g/l of arsenic trioxide. Arsenic trioxide is a recombination "poison" that inhibits nascent hydrogen atoms from combining to form diatomic gas. This process enhances the ingress of atomic hydrogen into the alloys. A 20 mA DC current was then applied to a cylindrical-shaped lead (Pb) anode at room temperature. This resulted in a current density of approximately 0.7 ma/cm² (4.5 ma/in²) for these notch tensile bars, which have a surface area of 30.2 cm² (4.68 in²). The electrolytic charging was imposed for various lengths of time, and notch tensile tests were conducted immediately after each charging to determine the extent of hydrogen embrittlement. The embrittlement index (EI), which is commonly used to describe the degree of embrittlement (ref 15), is defined as:

$$EI = (1 - NTS/NTS_0) \times 100 \quad (1)$$

where NTS and NTS₀ are the notch tensile strengths in the hydrogen-charged and the hydrogen-free specimens, respectively. A plot of the EI versus charging time was developed to determine an appropriate charging time for subsequent testing. (Note: The acronym EIs will be used to represent embrittlement indices throughout the rest of this paper.)

Notched Tensile Testing

The mechanical properties most affected by hydrogen embrittlement are notch tensile strength and measures of ductility (i.e., reduction in area or elongation) (ref 16). Hydrogen's effect on notch tensile strength is most pronounced at room temperature and at very slow strain rates (ref 17). Notch tensile tests were conducted on uncharged notched tensile bars to establish baseline, unembrittled, notched tensile data. Notch tensile tests with slow strain rates (i.e., 3.0 x 10⁻⁶/sec.) were used to determine the degree of embrittlement.

Grain Size

To determine the prior austenitic grain size, specimens were polished and etched using an aqueous solution of 1% picric acid and sodium tridecylbenzene sulfonate heated to 100°C (ref 18). ASTM grain size measurements were then obtained for each steel. Grain sizes were nearly identical for each of the four steels—showing fine grain structures measured at ASTM Grain Size Numbers 9 and 10. Therefore, grain size is not considered a factor for hydrogen embrittlement susceptibility in this investigation.

X-ray Diffraction/Energy Dispersive X-Ray (EDX) Analysis

X-ray diffraction was conducted to determine the presence of vanadium carbide, which was a possible trap site for hydrogen in the A723 steel samples. The carbide particles were electrolytically extracted using anodic dissolution procedures (refs 19-21). An A723 specimen constituted the anode in a solution of 7% vol. HCl in methanol and was dissolved with a current of 400 ma at 6v DC. After the steel anode was dissolved, the solution was decanted and allowed to evaporate; the black powder residues were then collected. An EDX spectrum of the elements

found in the residue helped to narrow the search; the identification was then made by x-ray diffraction.

Hydrogen Extraction Study

Hydrogen extraction measurements were conducted to determine how trapping affected the A723 and 4340 steels after charging. A microprocessor-controlled hydrogen detector was used to analyze the concentrations of diffusible hydrogen, which were extracted and measured at 200°C (392°F). Notched tensile bars were first conditioned by a hydrogen relief heat treatment at 200°C for four hours to effectively eliminate (bake out) any diffusible hydrogen. All specimens were then electrolytically charged with hydrogen for exactly 15 minutes. Specimens were then prepared for analysis using the BWRA/IIW (British Welding Research Association and International Institute of Welding) cleaning technique (ref 22), which is a three-step process that eliminates water vapor or surface contaminants that could contribute to the hydrogen content and cause errors in the analysis.

The volume of extracted hydrogen at 200°C was measured, and the result was accumulated over a 1400 second (23.3 min.) period. After the 200°C hydrogen extraction described above, A723 specimens were also tested at 800°C (1472°F). The higher temperature extractions helped to evaluate the hydrogen concentration in deeper traps.

RESULTS

Electrolytic Charging—4340 versus A723

Figure 2, which contains a plot of EI versus charging time, was developed to determine an appropriate amount of electrolytic charging time to provide a good comparison of 4340 and A723 at the same high strength level. The data in Figure 2 indicate that the EIs for A723 were considerably lower than those for 4340 for times up to four hours. After four hours, both steels become saturated and their hydrogen embrittlement susceptibility converges. Thus, for a specific charging time, 4340 steel is significantly more susceptible to hydrogen embrittlement—having both higher EIs and lower notch tensile strengths. A charging time of 0.25 hour (15 minutes) was selected for further testing because this charging time resulted in the largest difference in hydrogen embrittlement susceptibility between the two steels. At this charging time, the mean EI for 4340 was 61.3%, which was significantly higher than A723's index of 5.8%.

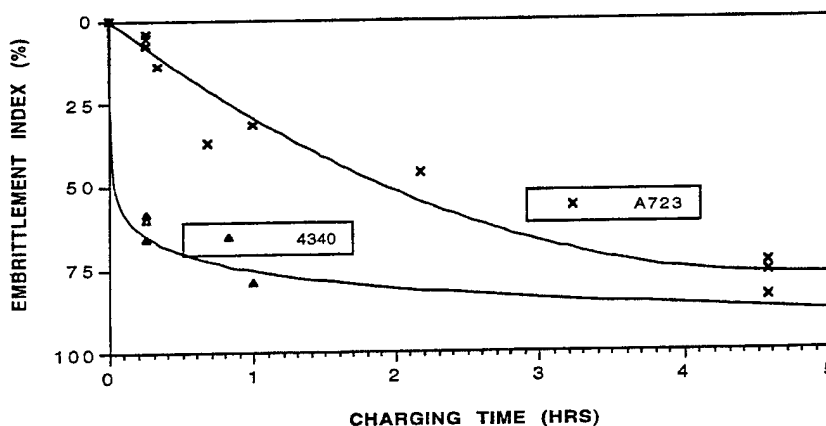


Figure 2. Embrittlement index versus electrolytic charging

Alloy Modifications

Table 3 compares the chemistries of the alloy modifications to the baseline alloys. Increasing the carbon in A723 steel to 0.40% and increasing the vanadium in the 4340 steel resulted in two steels with almost the same chemistries—with the exception of a higher nickel content and a slightly higher chromium and molybdenum content in the modified A723 steel.

Table 3. Chemistries of Baseline and Modified Steels (Wt. %)

| | Base A723 | Base 4340 | A723 Mod | 4340 Mod |
|----|-----------|-----------|----------|----------|
| C | 0.32 | 0.40 | 0.40 | 0.40 |
| S | 0.004 | 0.013 | 0.008 | 0.013 |
| P | 0.011 | 0.013 | 0.013 | 0.012 |
| Mn | 0.55 | 0.74 | 0.54 | 0.90 |
| Cr | 1.17 | 0.76 | 1.21 | 0.91 |
| Ni | 3.14 | 1.71 | 3.24 | 1.74 |
| Mo | 0.49 | 0.23 | 0.49 | 0.25 |
| V | 0.12 | trace | 0.12 | 0.12 |
| Si | 0.31 | 0.25 | 0.31 | 0.20 |

Notch Tensile Testing

Table 4 summarizes notch tensile tests, notch tensile strengths (NTS), and EIs of the steels. The baseline for 4340 showed significant embrittlement with a mean EI of 61.3%; however, neither the baseline A723 nor the modified A723 (with an increased carbon level of 0.40%) significantly degraded from their uncharged values, with mean EI values of 5.8% and 3.7%, respectively. Modified 4340 (vanadium added to 0.12%) was intermediate, with an EI of 22.1%. This demonstrates that the addition of vanadium was beneficial because the mean EI for the modified 4340 decreased from 61.3% to 22.1%.

Table 4. Notch Tensile Tests, Mean Values, and Embrittlement Indices

| Steel | Mean Uncharged NTS (MPa) | Charged NTS (MPa) | EI | Mean EI |
|-----------------------|-----------------------------|----------------------|-------|---------|
| Base 723 | 2310 | 2212 | 4.2% | 5.8% |
| | | 2184 | 5.5% | |
| | | 2133 | 7.6% | |
| Base 4340 | 1980 | 824 | 58.5% | 61.3% |
| | | 798 | 59.9% | |
| | | 684 | 65.6% | |
| Mod A723 (0.40% C) | 2445 | 2393 | 2.0% | 3.7% |
| | | 2365 | 3.2% | |
| | | 2298 | 6.0% | |
| Mod 4340 (0.12% V) | 2107 | 1344 | 36.0% | 22.1% |
| | | 1943 | 7.7% | |
| | | 1453 | 31.0% | |
| | | 1815 | 13.8% | |

Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to examine fracture surfaces to determine the mode of fracture (whether ductile or intergranular) and the extent of hydrogen embrittlement. The baseline for A723, which had an EI of 4.9%, showed microvoid coalescence with no intergranular fracture (Figure 3). The baseline for 4340 was severely embrittled, with an EI of 65.5% (Figure 4).

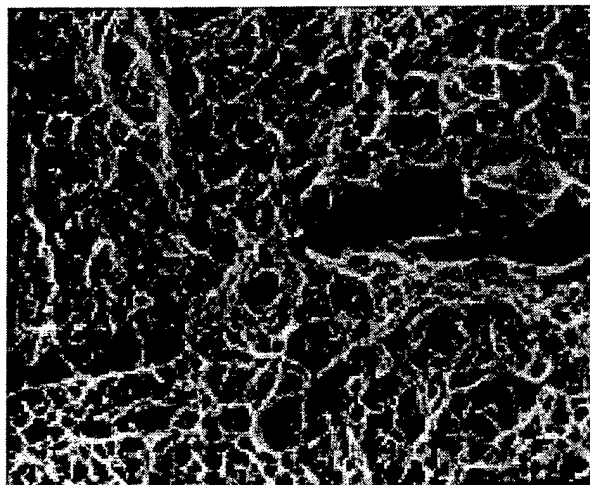


Figure 3. SEM at 500X, Base A723

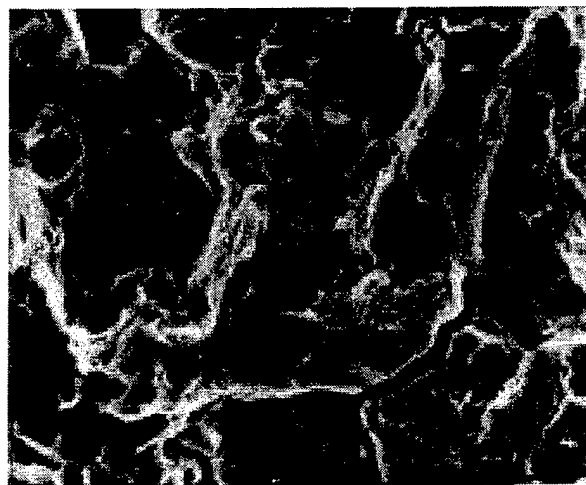


Figure 4. SEM at 2500X, Base 4340

SEM of Base 4340 at 10X (Figure 5) showed areas [A] of severe embrittlement and a complete intergranular fracture adjacent to approximately 80% of the notch circumference, with inward penetration of approximately 1.25 mm (0.05 in.) or approximately 40% of the radius. Modified A723, which had an EI of 3.3%, showed no intergranular areas on the fracture surface (Figure 6).

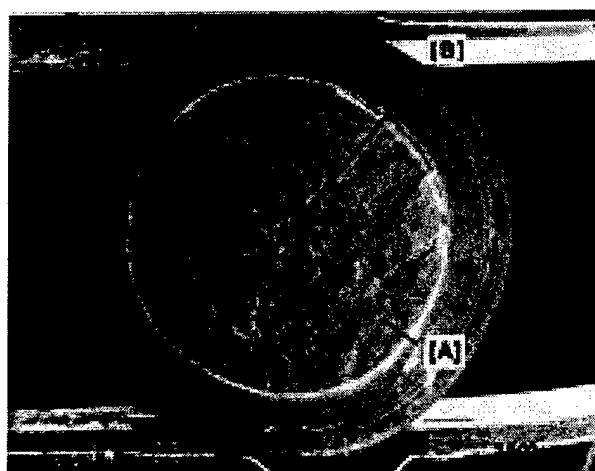


Figure 5. SEM at 10X, Base 4340

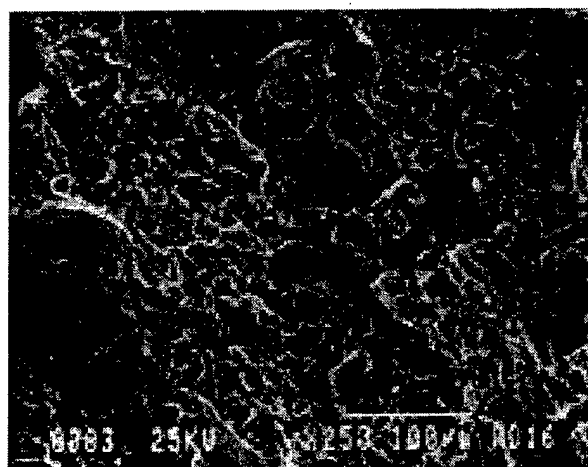


Figure 6. SEM at 250X, Modified A723

Modified 4340 (Figure 7), which had an EI of 13.8%, showed an outer intergranular ring near the notch diameter and microvoid coalescence in the inner region of the specimen. The intergranular outer area showed a slight penetration of 0.5 mm (0.02 in.) on the 6.35 mm (0.25 in.) diameter fracture surface. In summary, the SEM fractography generally agrees with the mechanical test data and the EIs of the four steels.

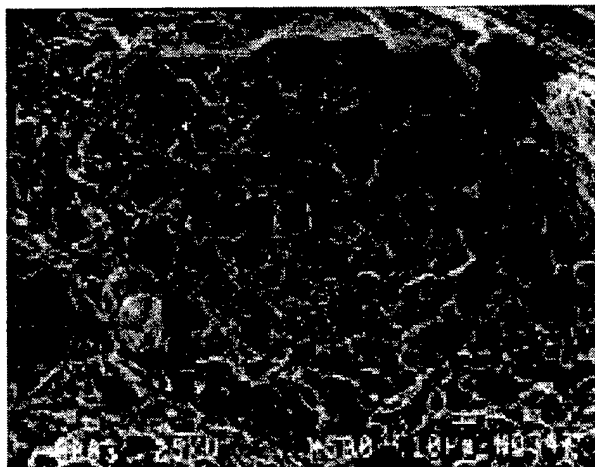


Figure 7. SEM at 500X, Modified 4340

EDX and X-ray Diffraction

X-ray diffraction and EDX (shown in Figure 8) identified the presence of second phases in the ASTM A723 steel samples. The EDX spectrum obtained from the electrolytic extraction residue showed two large peaks corresponding to vanadium and chlorine. The chlorine is from the HCl solution used during the extraction. The next largest peaks were carbon, molybdenum, silicon, and chromium. The x-ray analysis shown in Figure 9 clearly indicates that the extracted particles were vanadium carbide, V_4C_3 .

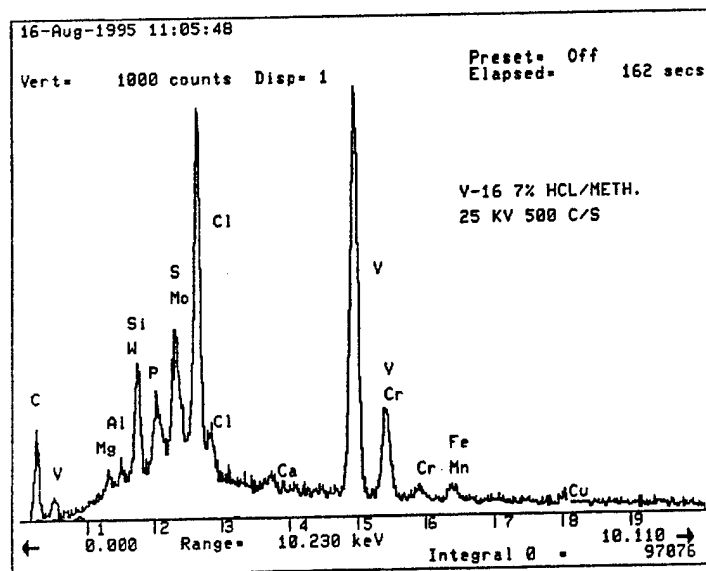


Figure 8. EDX spectrum of extracted residues

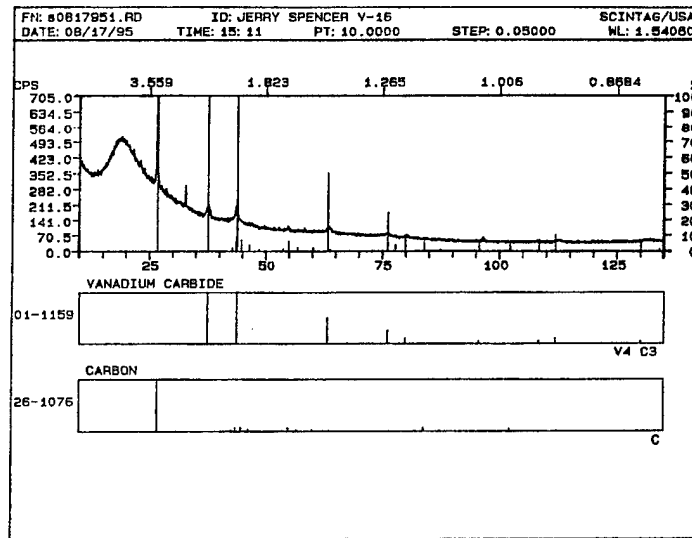


Figure 9. X-ray diffractograph of extracted residues

Hydrogen Extraction Study

To determine the possibility of hydrogen trapping, hydrogen extraction measurements were conducted to compare the A723 and 4340 steels. The results, which are presented in Table 5, show that the mean volume of hydrogen extracted from the 4340 steel (0.31 ml/100g) at 200°C was approximately three times that of the A723 steel (0.11 ml/100g). The significantly lower levels of hydrogen extracted from the A723 are attributed to vanadium carbide trapping the hydrogen. Because of this apparent trapping tendency, A723 specimens were tested at higher temperatures (800°C) after the hydrogen was extracted at 200°C.

Table 5. Hydrogen Extraction Results

| Modified (A723) | | |
|-----------------|---------------------------|------------------------------------|
| Spec. No. | Temperature of Extraction | Volume of H ₂ (ml/100g) |
| 5-1 | 200°C | 0.15 |
| 5-2 | 200°C | 0.08 |
| 5-3 | 200°C | 0.12 |
| 5-4 | 200°C | 0.05 |
| 5-5 | 200°C | 0.17 |
| Mean | 200°C | 0.11 |
| 5-6 | 800°C | 0.20 |
| 5-7 | 800°C | 0.18 |
| 5-8 | 800°C | 0.17 |
| Mean | 800°C | 0.18 |
| Baseline (4340) | | |
| Spec. No. | Temperature of Extraction | Volume of H ₂ (ml/100g) |
| 4-1 | 200°C | 0.34 |
| 4-2 | 200°C | 0.40 |
| 4-3 | 200°C | 0.29 |
| 4-4 | 200°C | 0.27 |
| 4-5 | 200°C | 0.25 |
| Mean | 200°C | 0.31 |

The higher temperature extractions helped to determine whether the A723 steel contained less apparent hydrogen than the 4340 steel or if the hydrogen in the A723 steel was trapped. When the mean value of the hydrogen concentrations extracted from the A723 steel at 800°C (0.18 ml/100g) was added to the mean value extracted at 200°C (0.11 ml/100g), the sum was 0.29 ml/100g. This shows good correlation with the 4340 steel (without the vanadium carbide traps), which had a mean value of 0.31 ml/100g.

In previous studies, the critical concentration of hydrogen required to induce hydrogen embrittlement was a strong function of the yield strength of steel alloys (Figure 10 [refs 23-25]). The “free” or diffusible hydrogen extracted from 4340 steel is enough to induce hydrogen embrittlement in this alloy. On the other hand, although the A723 steel contains essentially the same total level of hydrogen, it released only a fraction of the hydrogen upon heating at 200°C. These results indicate that the amount of “free” hydrogen in the A723 steel was not sufficient to induce any appreciable embrittlement.

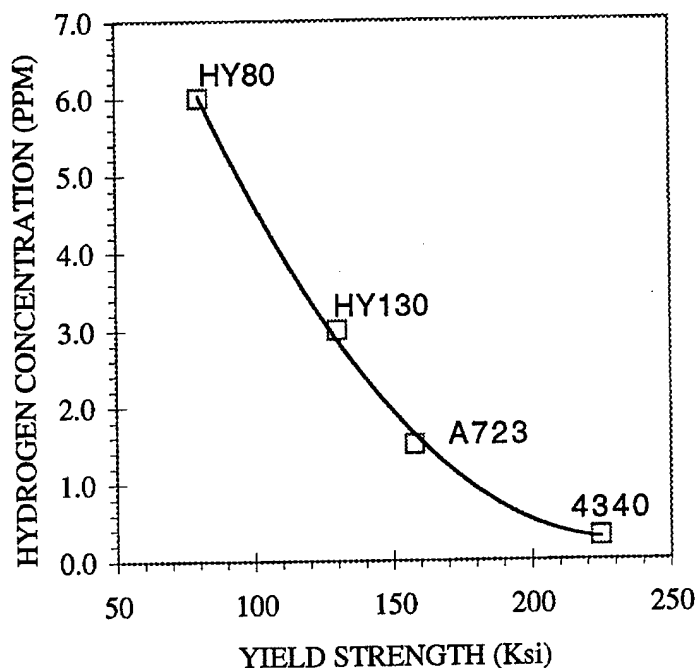


Figure 10. Critical hydrogen concentration versus yield strength

DISCUSSION

Discussion of Varying Alloying Elements

Although 4340 was embrittled (with an EI of 61.2%), the A723 steels were not embrittled. Because their corresponding strength levels and grain sizes were virtually identical, the difference in hydrogen embrittlement susceptibility can be attributed to the differences in alloying elements. The largest differences—and those chosen for further examination—were the carbon and vanadium levels. The ASTM A723 alloy has a carbon content of 0.32%, while 4340's content is higher at 0.40%. In addition, 4340 contained only trace amounts of vanadium, whereas the ASTM A723 has a vanadium level of 0.12%.

Modified A723

The carbon in ASTM A723 was increased from 0.32% to 0.40%—making it equivalent to that of AISI 4340—to determine if this would render the modified ASTM A723 steel more susceptible to hydrogen embrittlement. The notched tensile test data indicated that increasing the carbon resulted in a small increase in the notch tensile strength of the uncharged alloy. An SEM fractography of the charged alloy showed that this steel did not become embrittled, and that the EI did not degrade. These results mean that carbon does not cause a difference in hydrogen embrittlement susceptibility.

Modified 4340

To determine if the modified 4340 would become less susceptible to hydrogen embrittlement, vanadium was added to 4340—raising vanadium content from trace amounts to 0.12%, which is equivalent to the level of vanadium in ASTM A723 steel. This provided excellent control and allowed for a direct comparison of the effects of vanadium on the original 4340 and the modified 4340. The test results showed conclusively that modified 4340 (with an EI of 22.1%) was significantly less embrittled than the original 4340, which had an EI of 61.3%. SEM fractography agreed with the notch tensile testing (i.e., the extent and penetration of the hydrogen embrittled areas on the fracture surface correlated with the measured EIs).

In summary, the reduction of the EI from 61.3% to 22.1% was caused by the 0.12% vanadium addition. The additional difference between modified 4340's EI and modified A723's EI is believed to be a secondary effect caused by differences in molybdenum and the formation of Mo_2C traps in the modified A723 steel.

In an earlier empirical report (ref 1), Raymond suggested that increasing vanadium concentrations in high strength steels improved the hydrogen embrittlement susceptibility of the steels. However, his discussion suggested that vanadium's role was to refine the grain size. In addition, Raymond suggested that the effects of increasing the level of carbide formers was negligible. By contrast, this study demonstrates a strong correlation between hydrogen embrittlement susceptibility and the presence of vanadium carbides. These results suggest that the vanadium carbides act as effective hydrogen traps.

Hydrogen Trapping

This study was particularly interested in the trapping effect of carbides. Pressouyre and Bernstein (ref 2) found that titanium carbide particles act as strong hydrogen traps (with an interaction energy of 95 kJ/mol) and are irreversible traps at room temperature; however, titanium used as a substitutional atom is a reversible trap that has a relatively low interaction energy of 26 kJ/mol. The numerous studies on trap energies are summarized in Table 6.

Table 6. Hydrogen Traps and Interaction Energies

| Type of Trap | Interaction Energy | Matrix/Reference |
|---|--------------------|---------------------|
| Nd particle | 129 kJ/mol | Iron (ref 28) |
| TiC particle | 95 kJ/mol | C-Mn Steel (ref 2) |
| Al ₂ O ₃ particle | 79 kJ/mol | C-Mn Steel (ref 29) |
| MnS inclusion | 72 kJ/mol | C-Mn Steel (ref 30) |
| Ti substitutional atom | 26 kJ/mol | C-Mn Steel (ref 10) |
| Grain boundary | 59 kJ/mol | Iron (ref 9) |
| Grain boundary | 26 kJ/mol | C-Mn Steel (ref 28) |
| Dislocation core (mixed) | 59 kJ/mol | C-Mn Steel (ref 6) |
| Dislocation | 26 kJ/mol | Iron (ref 7) |
| Dislocation | 26 kJ/mol | C-Mn Steel (ref 28) |

Olson et al. (ref 14) investigated several second phase particles in steel to determine their interaction energy with hydrogen. One of these particles—Ce₂O₃, a rare earth oxide—was found to have the highest binding energy—followed by (in order of decreasing energy) TiC, Y₂O₃, VC, NbC, and Mo₂C. The binding energy of 60 kJ/mol for a dislocation or a grain boundary is generally regarded as the typical limiting value of a reversible trap (ref 14). A reversible trap with a binding energy lower than 60 kJ/mol cannot prevent hydrogen cracking because the trapped hydrogen will be picked up by moving dislocations and will eventually be delivered to crack initiation sites (refs 14, 26). The preferred traps are irreversible traps (i.e., those with binding energies greater than 60 kJ/mol) (refs 14, 27).

Vanadium carbide has a face-center-cubic NaCl-type structure (refs 31, 32), and, ideally, vanadium carbide should be present as VC. However, in most cases, a significant portion of the lattice is deficient in carbon—with some of the carbon sites empty. Although several carbon-deficient carbides exist (e.g., V₄C_{2.67}, V₄C₃, and V₈C₇ [ref 33]), V₄C₃ predominates in steel (ref 31) and was the vanadium carbide found via x-ray diffraction during this study. The empty carbon sites of the V₄C₃ may be the physical trap sites for diffusing hydrogen. Vanadium has five electrons (i.e., 3d³ and 4s²) in its outer electron shells that are available for bonding with the four carbon valence electrons. This leaves an extra (or unbonded) vanadium electron, which may be an attractive hydrogen trap site (ref 28).

Yoshino (ref 34) found that incoherent carbides (such as chromium carbide) increased the susceptibility of stress corrosion cracking (which, in this case, is synonymous with hydrogen embrittlement). Yoshino also found that fine coherent carbides (such as molybdenum carbide, vanadium carbide, titanium carbide, and niobium carbide) helped promote resistance to stress corrosion cracking. The presence of fine particles (i.e., less than 50 angstroms in diameter) of vanadium carbide, V₄C₃, in steels containing 0.2% C and vanadium greater than 0.10% were observed under transmission electron microscopy (TEM) by Aoki and Tanino (ref 10). These particles were coherent and formed parallel to {100} planes in the iron matrix.

In this study, it was found that vanadium carbides significantly reduced hydrogen embrittlement susceptibility. Vanadium carbide traps are classified as relatively strong irreversible traps (refs 31, 35). In addition, fine vanadium carbide particles precipitate coherently

with the steel lattice and are finely and homogeneously dispersed within the lattice. As a result, this distribution of hydrogen traps disperses the hydrogen and suppresses the concentration of hydrogen in any one area—thereby reducing the susceptibility to hydrogen-induced damage. Conversely, incoherent traps result in less cohesive strength and more areas where hydrogen and segregating impurities can congregate (ref 36).

In general, smaller and round, nonelongated inclusions are beneficial, and large grain sizes are detrimental because the associated lower grain boundary area provides fewer trapping sites—thereby increasing the probability that the concentration of hydrogen trapped on grain boundaries will reach its critical value. In addition, a nonhomogeneous distribution of defects or segregation favors large local hydrogen concentrations—with the accompanying deleterious effects. One way to avoid segregation is to produce stable carbides that do not dissolve and reprecipitate in the temperature range of service. Vanadium, titanium, or molybdenum alloy additions are ideal for this. Another parameter is precipitate coherency; incoherent interfaces offer less cohesive strength and are usually not distributed homogeneously—thereby providing more room for undesirable segregating impurities (ref 36).

In summary, the desirable characteristics for traps are rounded, small, coherent particles; a sufficient quantity of beneficial traps (to delay the time for the saturation); an irreversible character; and a homogeneous distribution.

Vanadium Carbides, Thermodynamics, and Kinetics

The ease with which vanadium carbide (V_4C_3) is formed—or the extent of the driving force of this reaction—is given by ΔG (the Gibbs free energy of formation), as follows:

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

where H = enthalpy, S = entropy, and T = temperature.

At 25°C (298°K), with values taken from thermo-chemical tables (ref 37):

$$\begin{aligned} \Delta G_{V-C@298^\circ K} &= -100.9 \text{ kJ/mol} - (298^\circ K)(0.0276 \text{ kJ/}^\circ\text{mol}) \\ \Delta G_{V-C@298^\circ K} &= -109.1 \text{ kJ/mol} \end{aligned} \quad (3)$$

This is a relatively large, negative, free energy and indicates a stable vanadium carbide. As the temperature at which this reaction takes place increases, the free energy or driving force also increases with a positive entropy (as shown in this case). By contrast, the formation of iron carbide (Fe_3C)—which is a competing reaction with the vanadium carbide reaction—the free energy of formation at 25°C (298°K) is:

$$\begin{aligned} \Delta G_{Fe-C@298^\circ K} &= +25.1 \text{ kJ/mol} - (298^\circ K)(0.1047 \text{ kJ/}^\circ\text{mol}) \text{ (ref 37)} \\ \Delta G_{Fe-C@298^\circ K} &= -6.1 \text{ kJ/mol} \end{aligned} \quad (4)$$

The formation of iron carbide is a factor of 18 times less favorable than the formation of vanadium carbide.

The formation of vanadium hydride is another reaction of interest. The free energy of formation at 300°C (573°K) is:

$$\Delta G_{V-H@ 573^{\circ}K} = -0.75 \text{ kJ/mol (ref 38)} \quad (5)$$

This is approximately two orders of magnitude less than the vanadium carbide reaction. Good steel-making practices typically take measures to reduce hydrogen to the barest minimum (usually <1.0 ppm), and the possibility of a vanadium-hydrogen reaction at this level is very unlikely. After the steel cools through a favorable temperature range of 720°C to 550°C for the vanadium-carbon reaction to occur, the vanadium carbide is formed. If this steel is then exposed to hydrogen, there is no longer any vanadium for vanadium hydride formation.

Kinetics may also play an important role in the formation of vanadium carbides. The kinetics of this reaction are governed by the mobility of the carbon atom to reach a vanadium atom in iron. This reaction is expressed by the Arrhenius relationship for diffusivity:

$$D = D_0 \exp(-Q/RT) \quad (6)$$

where D_0 = pre-exponential constant and Q = activation energy. With the values for D_0 and Q taken from referenced handbooks, the diffusivity for carbon in iron at 700°C is:

$$D_{\text{Carbon}@ 700^{\circ}C} = 5.76 \times 10^{-7} \text{ cm}^2/\text{sec (refs 37, 39)} \quad (7)$$

However, the diffusivity for vanadium in iron at 700°C is:

$$D_{\text{Vanadium}@ 700^{\circ}C} = 7.90 \times 10^{-13} \text{ cm}^2/\text{sec (refs 37, 39)} \quad (8)$$

Vanadium is primarily added to steel for grain size refinement to suppress grain growth. This is brought about by the fine vanadium carbide particles that are very stable, do not dissolve, and are not solutionized at temperatures less than 1200°C (ref 40), which is well above the normal heat-treatment temperatures. The presence of these finely dispersed vanadium carbide particles pin (or prevent) grain growth. Vanadium carbide may form either during slow cooling after melting in the 720°C to 550°C range (ref 31) or during a temper in the same temperature range (ref 28). An important effect of vanadium is that it induces resistance to softening at high temperatures—as long as the steel has been heat-treated in the ranges described above to form the vanadium carbide and absorb it into solid solution (ref 41). Consequently, vanadium steels may be used in elevated temperature applications.

Summary

The experimental evidence described earlier demonstrates that adding vanadium to 4340 significantly decreases hydrogen embrittlement susceptibility. The basis for this improvement was determined to be the beneficial effect of vanadium carbides, which trap diffusible hydrogen. This mechanism effectively reduces the hydrogen concentrations at potential crack sites—thereby reducing hydrogen embrittlement susceptibility. Thus, trapping constituents such as vanadium

carbides—or the even stronger trapping rare earth elements—can be designed as steel alloy additions that reduce or manage the problem of hydrogen embrittlement susceptibility.

CONCLUSIONS

1. Hydrogen-charged 4340 steel became heavily embrittled, with an EI of 61.2%, while A723 did not embrittle under identical conditions. Because the strength levels and grain sizes were identical for the A723 and the 4340, the difference in hydrogen embrittlement susceptibility was attributed to differences in the levels of alloying elements.
2. A 0.40% carbon level was not responsible for 4340's greater susceptibility to hydrogen embrittlement.
3. Adding vanadium to 4340 significantly improved its resistance to hydrogen embrittlement; this was subsequently found to be the cause of the susceptibility difference.
4. Hydrogen extraction studies demonstrated that vanadium carbides act as beneficial traps for diffusible hydrogen. The significantly lower levels of hydrogen extracted from A723 can be attributed to hydrogen trapping by vanadium carbide.
5. Vanadium (in the form of vanadium carbide, V_4C_3) was identified in the A723 steel by x-ray diffraction. V_4C_3 traps effectively reduced the hydrogen concentrations at the crack sites—thereby reducing hydrogen embrittlement susceptibility.
6. Notch tensile testing at slow strain rates was shown to be a reliable and effective method for measuring the extent of hydrogen embrittlement; this method was also ideally suited for comparison testing. The EI provided an excellent quantitative measure of the degree of embrittlement.
7. Designers or specifiers of gun steel material should not use AISI 4340 because of its high sensitivity to hydrogen embrittlement; they should use ASTM A723 or 4340 steels that have vanadium additions such as 300M (ref 42) or 4340M (ref 43).

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